ENAMELS

UDC 666.293:669.14:66.081:546.27

BORONIZING AS A NEW METHOD FOR TREATMENT OF STEEL FOR ONE-COAT ENAMELING

A. P. Zubekhin,[1] N. V. Veropakha,[1] and E. A. Yatsenko[1]

Translated from Steklo i Keramika, No. 5, pp. 30 – 32, May, 2000.

An efficient method is developed for preparing steel surface before single-coat enameling which involves boronizing in solid solutions, making it possible to shorten the process of pretreatment of the metal and make it more efficient without using special equipment.

The development and implementation of resource-saving technologies is especially important in the conditions of market economics with the view of decreasing production cost and improving product quality.

One of the fuel- and energy-consuming industrial sectors is the production of enameled articles, which involves double and sometimes even triple firing, which substantially increases the cost of the products. Therefore, the development of an efficient method for one-coat enameling is a promising field. This problem can be solved by carrying out physicochemical research and developing glass matrices (frits) which combine the properties of both undercoat and cover enamels, as well as developing efficient technologies for preparing the steel sheet surface before enameling.

A specific feature of one-coat enameling consists in the fact that when this method is used, the coating does not contain the undercoat layer which is adhesive and, therefore, the one-coat enamel should combine the properties of both cover and ground coats and provide for strong adhesion to steel. Therefore, it is necessary to introduce compounds contributing to good adhesion to metal into the one-coat enamel composition. However, the introduction of adhesive oxide into the enamel composition does not guarantee the required strength of adhesion of the one-layer coating to steel and, consequently, its good quality [1, 2], since the strength parameters of the "metal – enamel coating" composition are determined by various physicomechanical (TCLE, contact wetting angle) and physicochemical (structure and properties of the transition layer) parameters. In this connection, one-coat enameling, in addition to the standard treatment, calls for additional treatment of steel, for instance, nickelizing, copper plating, and deposition of cobalt, antimony, or phosphate compound films [2, 3].

The process of preparation of steel surface for one-coat enameling usually consists in the following stages: degreasing (thermal or chemical), pickling, deposition of nickel film (or other film), and neutralizing. Furthermore, washing with water is necessary after each stage, and the water consumption is substantial, amounting to 50 – 70 liters per 1 m^2 of steel sheet surface [1]. In one-coat enameling, a developed metal surface relief is of great significance; therefore, such stages as pickling and nickelizing are determining. It is recommended to carry out pickling for longer periods in solutions with increased acid concentration (up to 20% HCl and up to 25% H_2SO_4) or in nitric acid, but this requires installing special devices intended for protection from emitted nitric oxides and utilization of the pickling bath waste (sludge) [2 – 5].

Thus, the traditional methods for treating steel surface before one-coat enameling represent a rather lengthy, labor-consuming, and complicated process accompanied by substantial losses of metal during deep pickling and by consumption of numerous expensive reactants.

In this context, it is important to develop new, more efficient methods for metal treatment for one-coat enameling. A satisfactory method can be boronizing of steel surface, which is used in machine building for diffuse alloying of products [6 – 8]. Taking into account the specifics of enameling and the requirements imposed on steel surfaces in enameling, this method of metal treatment cannot be used in enameling production without being modified. Therefore, we carried out research intended for the development of new, more efficient and less labor-consuming techniques for boronizing of metal, which would be suitable for enameling. The boronizing

[1] South-Russian State Technical University (NPI), Novocherkassk, Russia.

0361-7610/00/0506-0179$25.00

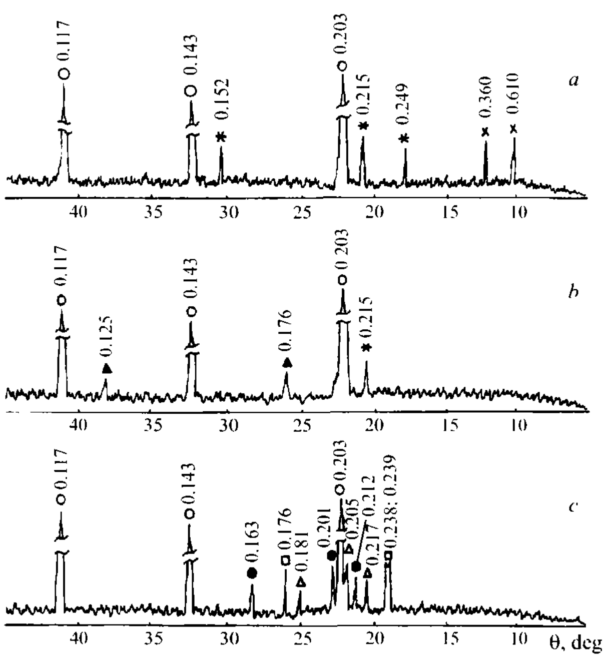

Fig. 1. X-ray patterns of 08kp steel samples treated by the traditional method (*a*), chemical nickelizing (*b*), and boronizing in solution (*c*): ○) α-Fe; *) FeO; ×) Fe_2O_3; ▲) Ni; Δ) $Fe_{23}B_6$; □) Fe_3B; ●) Fe_2B.

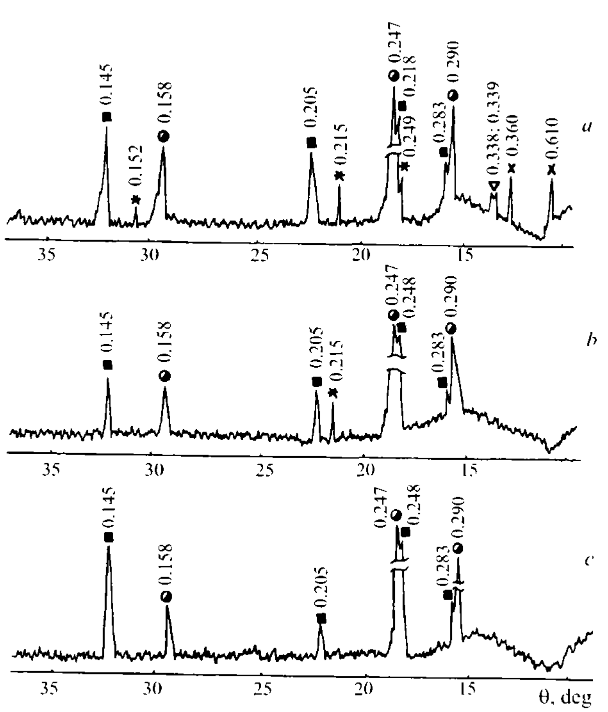

Fig. 2. X-ray patterns of "one-layer coating – steel" composite with steel treated by the traditional method (*a*), chemical nickelizing (*b*), and boronizing in solution (*c*): *) FeO; ×) Fe_2O_3; ■) $2FeO \cdot SiO_2$; ◑) $MnAl_2O_4$; ▽) $Fe_2Al_4Si_5O_{18}$.

methods known in machine building include boronizing in a gas medium, in dry master alloys, and in liquid media.

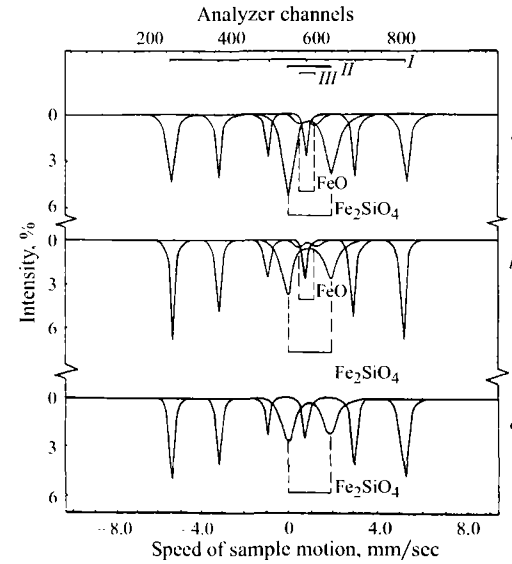

Fig. 3. NGR spectra of "one-layer coating – steel" composite with steel treated by the traditional method (*a*), chemical nickelizing (*b*), and boronizing in solution (*c*): *I*) α-Fe; *II*) $2FeO \cdot SiO_2$; *III*) FeO.

The studies indicated that the liquid method of steel boronizing (in solutions of boron-containing compounds) is more promising than other boronizing methods. The development of boronizing solutions was focused on two directions: solutions based on borax and on boric acid. The optimum composition of the borax-based solution is as follows (wt.%): 7.0 borax, 0.6 potassium boron hydride, 0.6 potash; solution based on boric acid (%): 5.00 boric acid, 4.52 KOH, 10.08 aluminum nitrate.

Simultaneously with studying the compositions of steel-boronizing solutions, various conditions of the boronizing process were investigated to select the optimum mode. Steel samples (grade 08kp) were placed in a cold furnace, heated to a prescribed temperature, held at this temperature for 5 – 10 min, and fully immersed in one of the prepared solutions (the solutions were at room temperature). The samples were held in the solution for a certain time needed to produce a boride film of the necessary thickness on the metal surface. After that the samples were washed and quickly dried at 70 – 100°C. It was established that the optimum heating temperature for steel was 400°C, and the optimum duration of holding in the solution was 10 – 15 min. In boronizing steel in the solution of the optimum composition according to the developed technology, the smoothest and most lustrous metal surface was obtained, which upon enameling exhibited high-quality one-layer coating.

The study of the mechanism of the boride layer formation on steel revealed that in the course of liquid boronizing in borax-based solutions, as a consequence of chemical reactions, active boron is formed near the steel surface, which then diffuses into steel and forms boride phases on the steel surface. For references purposes, the composition of the steel surface treated by different methods was studied using the

TABLE 1

Treatment method	Adhesion index, H, %, for sample extraction depth, mm							H_m, %
	1	2	3	4	5	6	7	
Standard treatment	100.0	99.2	96.1	79.0	69.0	65.1	64.3	81.81
Standard treatment (undercoat enamel)	100.0	100.0	89.8	79.1	74.4	74.0	72.3	84.23
Chemical nickelizing	100.0	100.0	100.0	98.4	96.1	90.7	88.9	96.30
Boronizing in solution	100.0	100.0	99.8	95.0	94.6	92.7	92.3	96.34

x-ray phase analysis. It was found that after the steel surface is treated by the standard method used in enameling or by chemical nickelizing, in addition to α-Fe, the oxide phases FeO and Fe_2O_3 as well are present on its surface (Fig. 1*a* and *b*), whereas after boronizing of steel, only boride phases ($Fe_{23}B_6$, Fe_3B, Fe_2B (Fig. 1*c*) were registered on the surface, and ferrous oxides were totally absent. This is the evidence of the formation of a continuous boride layer protecting the steel, which can later act as an adhesive link between the steel and enamel.

As a result of studying the transition layer adjacent to the one-layer coating – steel boundary using x-ray phase analysis (Fig. 2), nuclear gamma resonance (NGR) spectroscopy (Fig. 3), and electron microscope, the phase composition and the structure of this layer were identified. It was found that along with the phases Fe_2SiO_4 and $MnAl_2O_4$, iron oxides (FeO and Fe_2O_3) are also present in the transitional layer of steel treated by the standard method or by chemical nickelizing (Fig. 2*a* and *b* and Fig. 3*a* and *b*), which deteriorates the quality and the properties of the resulting one-layer enamel coat. At the same time, a correlation was established between the properties of one-layer coatings and the phase composition and structure of the transition layer: in boronizing of steel, a transitional layer consisting of Fe_2SiO_4, $MnAl_2O_4$, and aluminoboron-silicate vitreous phase is formed on the steel surface (Fig. 2*c* and Fig. 3*c*), which contributes to increased adhesion strength, heat resistance, and improvement of the coating quality. The presence of the transition layer of the specified composition on boronized steel is due to the reaction between reactive ferrous borides and the coating melt under firing, and formation of ferrosilicate phases. At the same time, the boron contained in the borides is oxidized with the melt oxygen and forms $[BO_4]^{5-}$ complexes which are incorporated into the glass structure and strengthen it. All this ensures an increase in the strength of adhesion of the one-layer coating to boronized steel.

It was found that boronizing of steel, compared to the standard steel treatment and chemical nickelizing, has a positive effect in the form of increased wettability, a more developed surface relief, a decreased degree of oxidation, and decarbonization of steel surface, which increases the strength of adhesion of the boronized steel to the one-coat enamel (Table 1) and improves the coating quality.

TABLE 2

Steel treatment method	Heat resistance of coating, °C	Luster of coating, %
Standard treatment	300	43.6
Chemical nickelizing	340	51.6
Boronizing in solution of optimum composition	360	52.0

Apart from the effect on the adhesion strength, the method of preliminary treatment of steel also has a substantial effect on such essential parameters of glass enamel coating as heat resistance and luster. The heat resistance of coatings was studied using the method of total sample heating [9], i.e., the maximum difference between the sample heating and chilling temperatures was determined, under which the glass enamel coating is not broken. The luster level was measured by the luster meter LÉÉM designed by NPI. The data of pretreatment of metal are given in Table 2.

Boronizing of steel to a great extent contributes to increased thermal resistance of one-layer coatings, compared to chemical nickelizing and especially compared to the standard metal treatment. This can be accounted for by an increase in the strength of adhesion of enamel to the boronized steel, as well as the formation of the aluminoboron-silicate vitreous phase in the transition layer, which acts as a "buffer" between the steel and the coating. The improvement of the quality of one-layer coats on boronized steel also leads to a certain increase in the coating luster.

Thus, it is established that the method of boronizing of metal in liquid media is promising for implementation in the one-coat enamel technology. The studies of the proposed method for steel boronizing in borax-based solutions demonstrated the possibility of producing single-layer coatings with better quality and properties than the coatings on steel treated by the standard method or by chemical nickelizing. The proposed method of boronizing makes it possible to shorten the process of pretreatment of metal and to make it more cost-effective without using additional equipment. This method has been implemented at enameling production enterprises.

REFERENCES

1. A. Petzold and G. Peshcmann, *Enamel and Enameling* [Russian translation], Metallurgiya, Moscow (1990).
2. *Enameling of Metal Articles* [in Russian], Mashinostroenie, Leningrad (1972).
3. V. Ya. Ioffe, "Technology of enameling of household gas and electric equipment," *Steklo Keram.*, No. 8, 25 – 27 (1993).
4. E. I. Litvinova, *Metal for Enameling* [in Russian], Metallurgiya, Moscow (1987).
5. V. P. Zakharov, M. E. Permyakova, and I. A. Glazycheva, "Certain peculiarities of steel intended for one-coat enameling," in: *Consumer Goods and Services Rendered to the Public* [in Russian], Sverdlovsk (1998).
6. L. G. Voroshnin and L. S. Lyakhovich, *Boronizing of Steel* [in Russian], Metallurgiya, Moscow (1978).
7. V. A. Zhabrev, V. G. Konakov, M. M. Pivovarov, et al. "Chemical reactions in borate melts," *Fiz. Khim. Stekla*, No. 2, 113 – 116 (1995).
8. G. V. Borisenko, L. A., Vasil'ev, L. G. Voroshnin, et al. (eds.), *Chemicothermal Treatment of Metals and Alloys* [in Russian], Metallurgiya, Moscow (1981).
9. V. E. Gorbatenko, V. A. Guzii, and A. P. Zubekhin, et al. (eds.), *Methods and Means of Analysis and Control in Glass Enameling* [in Russian], Novocherkassk (1995).